

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-176693

(43)Date of publication of application : 09.07.1996

(51)Int.Cl.

C22B 15/00

(21)Application number : 06-324420

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(22)Date of filing : 27.12.1994

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(54) COPPER RECOVERY

(57)Abstract:

PURPOSE: To separate and recover only copper by simple solvent extraction in the method for solvent-extracting the leachate of a mixed matte contg. cop per, nickel and cobalt by gaseous chlorine, by reducing the copper in the leachate to cuprous.

CONSTITUTION: A mixed matte contg. copper, nickel and cobalt is leached with gaseous chlorine, and copper is separated from nickel and cobalt and recovered by the solvent extraction of the obtained leachate. In this method, the copper ion in the leachate is reduced to cuprous ion, and the copper is extracted with a neutral extractant. Only copper is efficiently and selectively separated and recovered by this method. Besides, tributyl phosphate or trioctylphosphine is exemplified as the neutral extractant.

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CLAIMS

[Claim(s)]

[Claim 1]In a method of separating copper from nickel and cobalt by solvent extraction of a leaching solution obtained by exuding with gaseous chlorine in a mixed mat containing copper, nickel, and cobalt, and collecting, A recovery method of copper characterized by extracting copper using neutral extractant after returning a copper ion in said leaching solution to univalent.

[Claim 2]A recovery method of the copper according to claim 1 characterized by using tributyl phosphate or trioctyl phosphine as neutral extractant.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] From the leaching solution which oozed and carried out the mixed mat containing copper, nickel, and cobalt using gaseous chlorine, this invention separates only copper selectively by solvent extraction, and relates to the method of collecting.

[0002]

[Description of the Prior Art] Although sulfuric acid and ammonia may be used for processing of the mixed mat containing copper, nickel, and cobalt for extraction, the chloride solution of copper, nickel, and cobalt which exuded with gaseous chlorine and were obtained in the mixed mat is usually used in many cases.

[0003] The electrical conductivity of an electrolysis solution is high, and its electrolytic winning of nickel from that it exudes and the chloride solution of high-concentration copper, nickel, and cobalt can do a mat efficiently at the powerful oxidizing power of gaseous chlorine and a chloridation bath and cobalt is advantageous in cost, and also this is because a precise electrodeposited thing is obtained. It is also an advantageous point that a repetition of the gaseous chlorine which is a leaching agent can be performed.

[0004] The chloride solution of copper, nickel, and cobalt which were obtained by extraction by gaseous chlorine adds a raw material mat to this, carries out the precipitation of the copper from liquid in the form of a sulfide by a cementation reaction with nickel sulfides, and separates copper from nickel and cobalt. After carrying out oxidizing roasting of the copper settlings obtained by a cementation reaction, again, with sulfuric acid, they exude and electrolytic winning is carried out.

[0005] Thus, although separation with nickel and cobalt, and copper is possible, It was not avoided that a small amount of nickel and cobalt mix in the copper settlings which downstream processing is very complicated, and generates by a cementation reaction like

extraction / precipitation / extraction by this method, therefore copper perfect separation was difficult.

[0006]In order to separate copper from the leaching solution of a mixed mat, there is a method by solvent extraction besides what used the cementation reaction as mentioned above, and various examination is added from down stream processing being easy.

[0007]For example, generally acid extractants, such as the trade name LIX, are used as copper extractant. In acid extractant, it is said from the liquid of low pH that copper extraction separation is possible. However, the actual pH of the leaching solution which mixed the mat is less than zero in many cases, and recovery of copper from such extreme low pH is difficult. In extraction by acid extractant, since the pH of liquid falls as copper is extracted, in order to keep the pH of liquid constant, addition of neutralizers, such as NaOH and NH₃, is needed, and the accumulation to the leaching solution of the ingredient of these neutralizers poses a problem.

[0008]Use of TIOA [which is basic extractant] (Tri iso-octyl amine), and Alamine336 is also considered by recovery of copper from a leaching solution. Such extractants are called basic extractant and can extract the metal ion of an anion state. In the chlorine extraction solution of a mat, since copper forms shade complex ion with chlorine, copper extraction is possible.

However, in order that not only copper but cobalt may form shade complex ion with chlorine, there is a fault that both will be extracted by TIOA and cannot do mutual separation.

[0009]It is known that neutral extractants, such as TBP (Tri butyl phosphate) and TOPO (Tri octyl phosphine oxide), will not be concerned with the pH of liquid, but a metal ion can be extracted. Since such neutral extractants extract a metal ion in the form of a salt, extraction advances, so that the salt concentration of liquid is high. That the pH of the leaching solution of the mixed mat by gaseous chlorine is low means that the salt concentration of liquid is high, and it brings a desirable effect to extraction.

[0010]However, the partition ratio which such neutral extractant does not have the extractability to copper, and is defined by the ratio of the metallic ion concentration in the metallic ion concentration/aqueous phase in the organic phase after extraction is only a very small value called 10⁻¹ - 10⁻³. Therefore, copper extraction was not able to be performed, even if extraction of copper by these neutral extractant is difficult and it repeated the extract operation of a lot of extractants and multistage.

[0011]

[Problem(s) to be Solved by the Invention]An object of this invention is to provide how it dissociates selectively and solvent extraction with an easy process recovers only copper from the leaching solution which oozed and carried out the mat containing copper, nickel, and cobalt using gaseous chlorine in view of this conventional situation.

[0012]

[Means for Achieving the Goal]In a method of separating copper from nickel and cobalt by

solvent extraction of a leaching solution obtained by this invention exuding a mat containing copper, nickel, and cobalt with gaseous chlorine in order to attain the above-mentioned purpose, and collecting, After returning a copper ion in a leaching solution to univalent, a recovery method of copper extracting copper using neutral extractant is provided.

[0013]

[Function]The result of having examined various how this invention persons do solvent extraction of the copper from the leaching solution of the mixed mat by gaseous chlorine, After returning the leaching solution containing copper, nickel, and cobalt and changing copper into a univalent state, it found out that copper could be extracted selectively and efficiently by contacting neutral extractants, such as tributyl phosphate (TBP) or trioctyl phosphine (TOPO). [0014]Specifically, the mixed mat which contains copper, nickel, and cobalt first is exuded with gaseous chlorine. The main reaction which leaches copper in the mat by chlorine at this time is a reaction which copper sulfide reacts to chlorine and serves as a solution of CuCl_2 like the following reaction formula.

[0015]

[Equation 1] $\text{Cu}_2\text{S} + 2\text{Cl}_2 \rightarrow 2\text{Cu}^{2+} + 4\text{Cl}^- + \text{S}$ [0016]Therefore, the copper's in obtained leaching solution existence gestalt exists in the divalent state of Cu^{2+} . Although copper of this divalent state can hardly be extracted by neutral extractant, extraction by neutral extractant is attained by returning this and considering it as univalent.

[0017]This reduction operation is easily made by addition of the mat of a raw material, a copper metal, or bad second acid ion, etc. Whether the reduction reaction of $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ was completed should just check that ORP (oxidation-reduction potential) of liquid is 300 mV or less on silver / silver silver chloride electrode standard. Since a divalent copper ion is hardly extracted by TBP and TOPO, this reduction operation is important.

[0018]Thus, if the liquid by which copper was returned is contacted to neutral extractants, such as TBP and TOPO, only copper will be selectively extracted by the organic phase (extractant). Since neither TBP nor TOPO has the extraction capability to nickel or cobalt, it can leave nickel and cobalt in a leaching solution to the aqueous phase (leaching solution), and copper extraction selectivity is very high.

[0019]In the case of this solvent extraction, the concentration in particular of neutral extractants, such as TBP used for copper extraction, is not limited, and is diluted with kerosene etc., and if it is used by 10 - 100 volume % so that it may be used by the usual solvent extraction, there will be no problem in particular. However, when raising the concentration of neutral extractant, and much copper can be extracted in a little amount of organic solvents and real operation is considered, it cannot be overemphasized that it becomes advantageous.

[0020]Generally in the solvent extraction by neutral extractants, such as TBP and TOPO, it is

said that it is extracted in the form of a neutrality electrically salt like $M_m X_n$ (the metal ion and X which M wants to extract opposite negative ion, an example yes, Cl^-). Although it is thought by copper extraction that it is extracted in the form of CuCl_2 and CuCl , the combination of Cu and Cl in CuCl is considered to be what has the firm and high stability as a salt so that it may understand from the solubility to the water of CuCl being very small compared with CuCl_2 . Therefore, it is thought by returning in advance of extraction and making a copper's existence gestalt univalent that copper is efficiently extracted by neutral extractants, such as TBP and TOPO.

[0021] Back extraction of the copper extracted by neutral extractants, such as TBP and TOPO, can be carried out like the case where these extractants are usually used, using water. In this case, back extraction of the copper currently extracted by TBP or TOPO is carried out in the form of CuCl .

[0022] Since CuCl by which back extraction is carried out is poorly soluble at water, the aqueous phase after back extraction will be in the state where the powder of CuCl was suspended, and the powder of CuCl will be obtained, if this liquid is filtered and output is dried. On the other hand, if oxidizers, such as hydrogen peroxide and chlorine, are beforehand added to back extraction liquid (water) and back extraction operation is performed, back extraction of the univalent copper currently extracted by TBP and TOPO is carried out oxidizing to divalent, and it can be collected as solution of CuCl_2 .

[0023]

[Example]

The mixed mat (Cu:30.9%, nickel:29.0%, Co: 14.7%) containing example 1 copper, nickel, and cobalt was exuded using gaseous chlorine, and the leaching solution (Cu:9.9 g/l, nickel:9.3 g/l, and C_O_2 :4.7 g/l) was obtained.

[0024] Sodium sulfite was added to this leaching solution, and the oxidation-reduction potential of liquid was adjusted to 247 mV on silver / silver silver chloride electrode standard. Next, with the diluent (trade name Shellsol A), 50 ml of neutral extractant which adjusted TBP concentration to 40 volume % was added to 50 ml of this leaching solution, and it mixed well to it. Then, the solvent and remaining extraction liquid which extracted copper were separated, and back extraction of the solvent was carried out with tales doses of 0.1% H_2O_2 liquid.

[0025] As a result of analyzing the copper concentration of back extraction liquid, the copper quantity extracted by TBP is 3.1 g/l, and has extracted efficiently 30.8% of copper in a leaching solution. At this time, the extractability of nickel and cobalt is 0.01% or less, and was understood that copper selection extraction is possible.

[0026] The mixed mat (Cu:30.9%, nickel:29.0%, Co: 14.7%) containing example 2 copper,

nickel, and cobalt was exuded using gaseous chlorine, and the leaching solution (Cu:9.9 g/l, nickel:9.3 g/l, and C_O:4.7 g/l) was obtained.

[0027]Sodium sulfite was added to this leaching solution, and the oxidation-reduction potential of liquid was adjusted to 241 mV on silver / silver silver chloride electrode standard. Next, it was used for 50 ml of this leaching solution as it is, without diluting TBP, 50 ml of neutral extractant of TBP was added, and it mixed well. Then, the solvent and remaining extraction liquid which extracted copper were separated, and back extraction of the solvent was carried out with tales doses of 0.1%H₂O₂ liquid.

[0028]As a result of analyzing the copper concentration of back extraction liquid, the copper quantity extracted by TBP is 5.3 g/l, and has extracted efficiently 53.3% of copper in a leaching solution. At this time, the extractability of nickel and cobalt is 0.01% or less, and was understood that copper selection extraction is possible.

[0029]The mixed mat (Cu:30.9%, nickel:29.0%, Co: 14.7%) containing comparative example 1 copper, nickel, and cobalt was exuded using gaseous chlorine, and the leaching solution (Cu:9.9 g/l, nickel:9.3 g/l, and C_O:4.7 g/l) was obtained.

[0030]Solvent extraction operation was presented with this leaching solution as it was, without also performing pretreatment of what. The oxidation-reduction potential of this leaching solution is 558 mV on silver / silver silver chloride electrode standard, and the copper ion which exists in liquid is in a divalent state.

[0031]Next, with the diluent (trade name Shellsol A), 50 ml of neutral extractant which adjusted TBP concentration to 40 volume % was added to 50 ml of this leaching solution, and it mixed well to it. Then, the solvent and remaining extraction liquid which extracted copper were separated, and back extraction of the solvent was carried out with tales doses of 0.1%H₂O₂ liquid.

[0032]As a result of analyzing the copper concentration of back extraction liquid, the copper quantity extracted by TBP is 0.001 g/l, and it turned out that copper in a leaching solution is not extracted at all.

[0033]

[Effect of the Invention]According to this invention, by the solvent extraction using neutral extractant, copper can be selectively separated from nickel and cobalt, and copper can be efficiently collected from the leaching solution which oozed and carried out the mixed mat containing copper, nickel, and cobalt using gaseous chlorine.

[Translation done.]